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Etching process of silicon carbide from polysiloxane by chlorine

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ABSTRACT

The etching process of silicon carbide by dry chlorine was investigated as a function of etching temperature using a commercial available polymethyl(phenyl)siloxane resin. Results from etching rate show increasing etching temperature could lead to a change for etching mechanism from diffusion-controlling to interface reaction-controlling. The chlorination of β-SiC in this study should be managed at above 600 °C and can complete at 900 °C for 3 h. A pronounced core–shell structure was observed owing to the partial conversion. Silicon carbide derived carbons (SiC-DCs) are in highly microporosity, with single-modal pore size distributions at around 0.9 nm.

1. Introduction

In recent decades, Carbide derived carbons (CDCs) have received growing attentions for tunable pore structure and narrow pore size by selectively etching metal carbides or choosing suitable parameters [1–3]. Carbide species have been considered as one of the most important factors which can affect CDC structure and property. Previous studies have been generally carried out toward some binary metal carbides (SiC, TiC, WC, etc.) or ternary carbides (Ti_2AlC, Ti_3SiC_2, etc.), and it is demonstrated that these CDCs possess different pore structures and properties [4–9].

In comparison with other carbides, SiC is one of the most widely used carbides for CDCs growth because of its relatively low cost and numerous applications ranging from composites to electronics, wear-resistant components, micro-electro-mechanical systems. Silicon carbide derived carbons (SiC-DCs) are always characterized by huge surface area, large pore volumes and tunable microstructures. Besides, their pore size distributions are significant narrow, commonly in micropore ($\leqslant$2 nm) range, which makes SiC-DCs potential candidates for energy-related gas storage (H_2, CH_4) or CO_2 capture, electrode materials for supercapacitors. Nevertheless, the conversion and properties of SiC-DCs may vary a lot with different SiC species, such as particle size, phase and initial geometry or macrostructure [10–12,6,13].

Herein, we reported a novel fabrication of SiC-DCs from polysiloxane (PSO). PSO has been studied and adopted for precursor of SiOC ceramics for many years for its commercial availability, low cost, abundant species and convenient manipulation. According to our previous work [14,15], predominant SiC ceramics can be obtained by pyrolyzing PSO at over 1400 °C under vacuum. In comparison with conventional fabrications of SiC (e.g., chemical vapor deposition, sintering, carbothermal reduction), the compositions and structures of PSO-derived SiC may be well-controlled by changing pyrolysis temperatures and other schemes, which can further optimize the structures of SiC-DCs. Besides, the conversion from PSO to SiC can near net-shape, which makes it reality or easier to acquire carbons with complex shape. However, such work has hitherto not been reported. The etching process of PSO-SiC via chlorine is still unknown. The compositional and structural evolution of SiC from PSO as a function of etching temperature or time still requires further exploring, although some articles have reported the carbon coatings formed on bulk SiC ceramics [16], SiC powders [17] and SiC whiskers [18,19] via CDC techniques. To reveal the etching process of SiC powders from PSO, the etching rate of SiC particles at different temperatures or etching times was also investigated in this paper.

2. Experimental

2.1. Sample preparation

SiC ceramics were produced by pyrolysis of a commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin). The polysiloxane precursor was first cross-linked at 250 °C in air for 4 h, and crushed into powders by using a disintegrator. The powders (with particle sizes ranging from 150 to 250 μm) were placed in a graphite crucible and heated to 1200 °C for 2 h under

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nitrogen (99.999% pure) with a heating rate of 5 °C/min and then allowed to cool naturally. Subsequently, the SiOC was ball-milled to micron powders (<20 μm particle size) and thermal-treated at 1500 °C under vacuum for 6 h. To investigate the etching process, SiC powders were placed in a horizontal tube furnace (diameter 6 cm), purged in nitrogen flow, heated to temperature in the range of 600–900 °C with the rate of 5 °C/min and exposed to dry chlorine gas (15–20 cm^3/min) for different times (1–3 h).

2.2. Characterization methods

2.2.1. Compositional and structural analysis

Quantitative elemental analysis (EA) of the samples was performed on LECOCS600 for carbon in SiC ceramics. The perchloric acid dehydration gravimetric method was adopted for the determination of Si content. And the residue element is considered to be O. Given that the C atom should connect with itself or Si atom while O atom connects with Si atom only, atomic formula and calculated composition could be obtained according to Ref [20]. It is calculated that nearly 5.19 wt.% of the as-received SiC ceramics from PSO is assigned to free carbon. For CDCs, their compositions were determined by X-ray photoelectron spectroscopy (XPS) technique and X-ray spectrometer (EDS) technique. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a K-Alpha 1063 system (Thermo Fisher Scientific) with Al Ka radiation. Unless otherwise specified, the X-ray anode was run at 72 W and the high voltage was kept at 12.0 kV. The base pressure of the analyzer chamber was about 1×10^{-10} Pa. A whole spectrum scan (0–1400 eV) and regional scans of all the elements at a very high resolution were recorded for each sample. Binding energies were calibrated using the carbon 1s peak (C1s = 284.6 eV).

Infrared spectroscopy (IR) between 4000 and 400 cm^{-1} was carried out with a resolution of 4 cm^{-1} on a Thermo Niocolet Fourier Transform Spectrum, using the KBr disk method. X-ray diffraction (XRD) analysis was managed using a Rigaku diffractometer with Cu Ka radiation (k = 0.154 nm) operated at 30 mA and 40 kV. XRD patterns were collected using step scans, with a step size of 0.01° (2θ) and a count time of 2 s per step between 10 (2θ) and 90 (2θ) degrees. Raman spectra were recorded with a LABRAM-HR (JOBIN YVON) microspectrometer using an argon-ion laser (514.5 nm, ~1 μm lateral spot size). Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449C instrument, and carried out with a minimal ambient air flow rate of 40 ml/min in the temperature range between 25 and 800 °C, with a heating rate of 5 °C/min.

Sample morphology and composition was characterized using a HITACHI FEG S4800 scanning electron microscope operating at 10 kV equipped with an energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) samples were prepared by dispersing powders in ethanol and placing the solution over a copper grid. TEM measurements were performed using a JEOL JEM2100F microscope operating at 200 kV.

2.2.2. Gas sorption measurement

N_2 adsorption–desorption isotherms were obtained using a Quantachrome instrument at 77 K. Brunauer–Emmett–Teller (BET) analyses were used to determine the total specific surface area (S_{BET}). The quenched solid density functional theory (QSDFT) method was used to analyze pore size distributions (PSDs) and pore volume.

3. Results and discussion

3.1. Etching mechanism of SiC ceramics from PSO

To investigate the etching mechanism of SiC powders from PSO, the reaction progress was determined gravimetrically, which may be more suitable for anomalous SiC powders compared with the mechanism studies by measuring the CDC thickness at different etching time. The mass of the precursor carbide was measured before the experiment and after the reaction (after the reactor had been cooled down). Partially reacted carbides were not further used for the kinetic study, i.e. the reaction time was varied based on experiments with fresh SiC. If it is assumed that the recorded loss of mass results only from silicon, which is etched from the carbide, hence that no carbon is etched and that no re-deposition occurs, the etching rate is given by:

$$r = \Delta m / M_{\mathrm{Si}} \cdot t \cdot (m_0 - m_{c(f)}) \tag{1}$$

with r: etching rate in 10^{-6}·mol/kg/s); t: the time in s; m_0: initial mass in kg; M: molar mass in kg/mol; $m_{c(f)}$: the mass of free carbon in SiC before etching in kg.

The etching rate of SiC at different temperatures is calculated by Eq. (1). A variation of etching rate as a function of etching time is depicted in Fig. 1. All curves show a rise at elevated etching time owing to the increase of contact surface between reactants. The slope coefficient k_l is obtained by linear fitting to reveal the trend. It is noted the etching rate for 600 °C is much small (fit linear k_l = 0.02), indicating that the etching reaction should be managed at above 600 °C. From our knowledge and previous studies [18], it can be considered that the etching reaction at 600 °C obeys a diffusion-controlled mechanism. Similarly, Gogotsi et al. also found the CDC films in nanometers can form on β-SiC micron particles after 27 h etching in Ar–3.5% Cl_2 at 600 °C [17]. For β-SiC whiskers, the thickness is too thin to estimate precisely at 600 °C for kinetic studying [18]. When it temperature reaches 900 °C, a big increase for the etching rate is observed at constant reaction time compared with that for 600 °C, the fit linear k_l reaches 0.8. Nevertheless, the two curves for 600 °C and 900 °C display a different trend, implying that much shorter etching time is needed for complete conversion because of quick reaction at 900 °C. Thereby, the interface reaction-controlled mechanism can be concluded for the chlorination at this temperature. At 750 °C, the etching rate almost climbs linearly (fit linear k_l = 0.4) with the reaction time, possibly suggesting a intermediate state for the etching mechanism of β-SiC particles in this study. That means a longer reaction time is required than the etching process at 900 °C, but much shorter than that for 600 °C.

3.2. Compositional evolution of SiC ceramics from PSO

To explore the compositional evolution of SiC at different temperatures, we managed the chlorination with constant time (3 h). For this study, X-ray photoelectron spectroscopy (XPS) and X-ray spectrometer (EDS) technique was used, as seen in Fig. 2. The XPS survey scan of the initial sample exhibits major peaks assigned to the C1s (~284 eV), O1s (~532 eV), Si2s (~153 eV) and Si2p (~100 eV) photoelectrons. After chlorination at 600 °C and above, the Cl2p peak (~200 eV) and Cl2s peak (~270 eV) were observed. The C1s became the most prominent feature at etching temperatures greater than 750 °C, with two discernible peaks belonged to O1s and Cl2p respectively. However, data from Table 1 shows that the Si content by EDS method still reaches 8.34 at.%, indicating that the conversion is partial at below 900 °C for 3 h, with increasing degree at elevated etching temperatures.

Infrared (IR) is useful for analysis of silicon contained bonding (Si–O, Si–C). Besides, this technique is often adopted to characterizing the functional groups on the surface of carbon materials. Fig. 3 shows a typical infrared (IR) spectrum of SiC as well as spectra of the products following the chlorine etching process. As expected, the SiC sample shows a sharp peak at 824 cm^{-1}, which is assigned to the ν(Si–C) absorptions. Besides, another weak and broad absorption centered at 1041 cm^{-1}, characteristic of